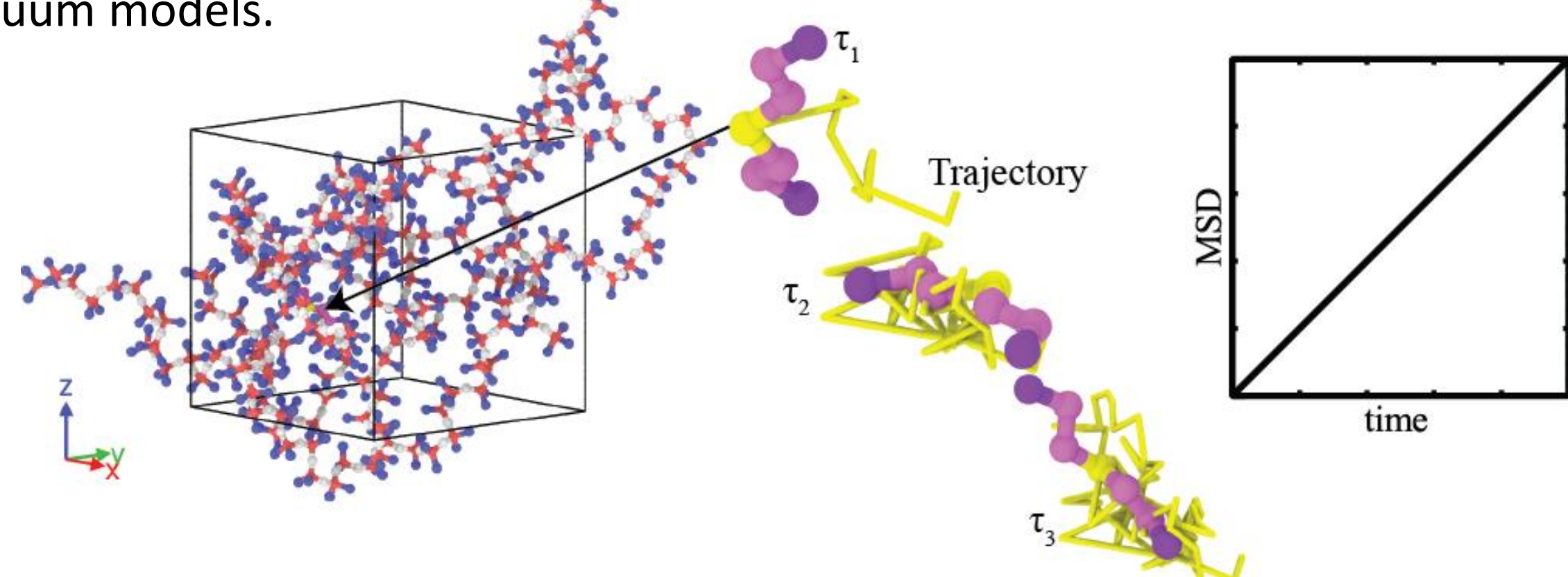


## Scope

As part of an ongoing effort to distinguish similarities and differences between chemical warfare agents (CWA) and their simulants, methods such as molecular dynamics (MD) provide direct analysis of thermodynamic and transport properties in polymeric materials. Obtaining diffusivities and mechanisms associated with diffusion of agents and simulants in homogeneous polymer materials such as polydimethylsiloxane (PDMS) provide a path towards a greater understanding in heterogeneous military coating systems. This information can assist in validation of predicted transport properties from continuum models.



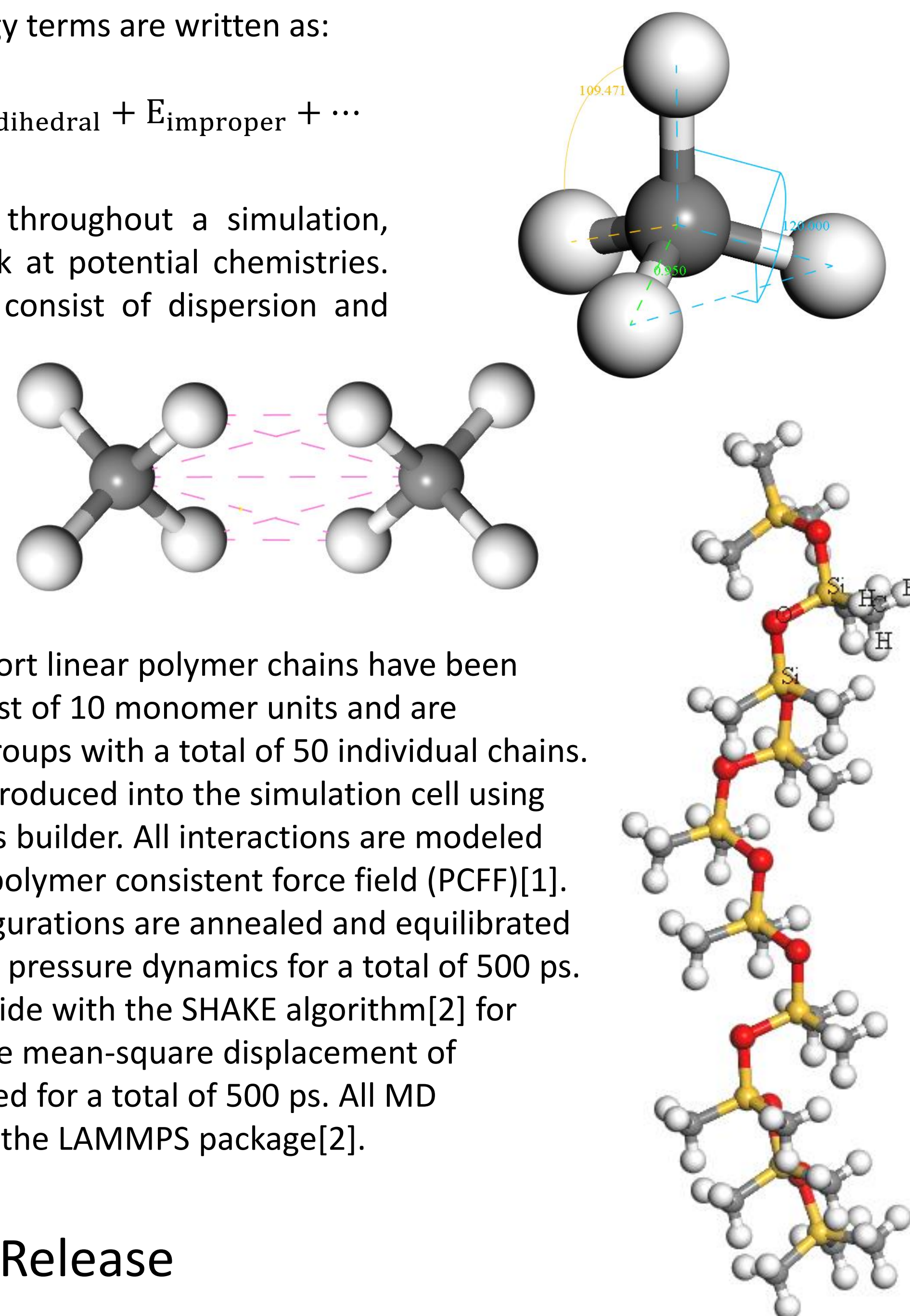
## Molecular Dynamics

Classical simulations of atoms/molecules imply that dynamics can be appropriately captured using Newtonian mechanics. This ultimately depends on the ability to describe the interactions between atoms/molecules properly. Typically for polymeric and organic materials, force fields are used to treat interactions. The energy between atoms/molecules in force fields are described using bonded and non-bonded interactions. The bonded energy terms are written as:

$$E_{\text{bonded}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}} + E_{\text{improper}} + \dots$$

The bonded terms are fixed throughout a simulation, which limits the ability to look at potential chemistries. The non-bonded interactions consist of dispersion and electrostatic interactions:

$$E_{\text{non-bonded}} = E_{\text{vdw}} + E_{\text{coul}}$$



## Simulation Details

As a first approach, relatively short linear polymer chains have been studied. The chain lengths consist of 10 monomer units and are terminated with three methyl groups with a total of 50 individual chains. The penetrant molecules are introduced into the simulation cell using the Materials Studio Amorphous builder. All interactions are modeled using the parameters from the polymer consistent force field (PCFF)[1]. The PDMS with penetrant configurations are annealed and equilibrated using constant temperature and pressure dynamics for a total of 500 ps. A timestep of 1 fs is used alongside with the SHAKE algorithm[2] for numerical integration. Finally the mean-square displacement of penetrant molecules is calculated for a total of 500 ps. All MD simulations are performed with the LAMMPS package[2].

## Diffusivity from mean-square displacement

The penetrant diffusivity in PDMS can be related to the mean-square displacement (MSD) by :

$$\lim_{t \rightarrow \infty} D = \frac{1}{6t} \frac{\langle |r(t_0 + t) - r(t_0)|^2 \rangle}{\text{MSD}} \quad \text{eq. 1}$$

The MSD for varying weight percent (wt. %) of HD at 298K is shown in fig. 1, the slope (blue line) is proportional to the diffusivity. Similarly in fig. 2 the MSD for CEES is shown.

Resulting diffusivity as a function of weight percent HD and CEES are shown in Table 1. The diffusivities for both HD and CEES decrease linearly as molecular weight of the penetrant decreases. The values for HD and CEES are similar.

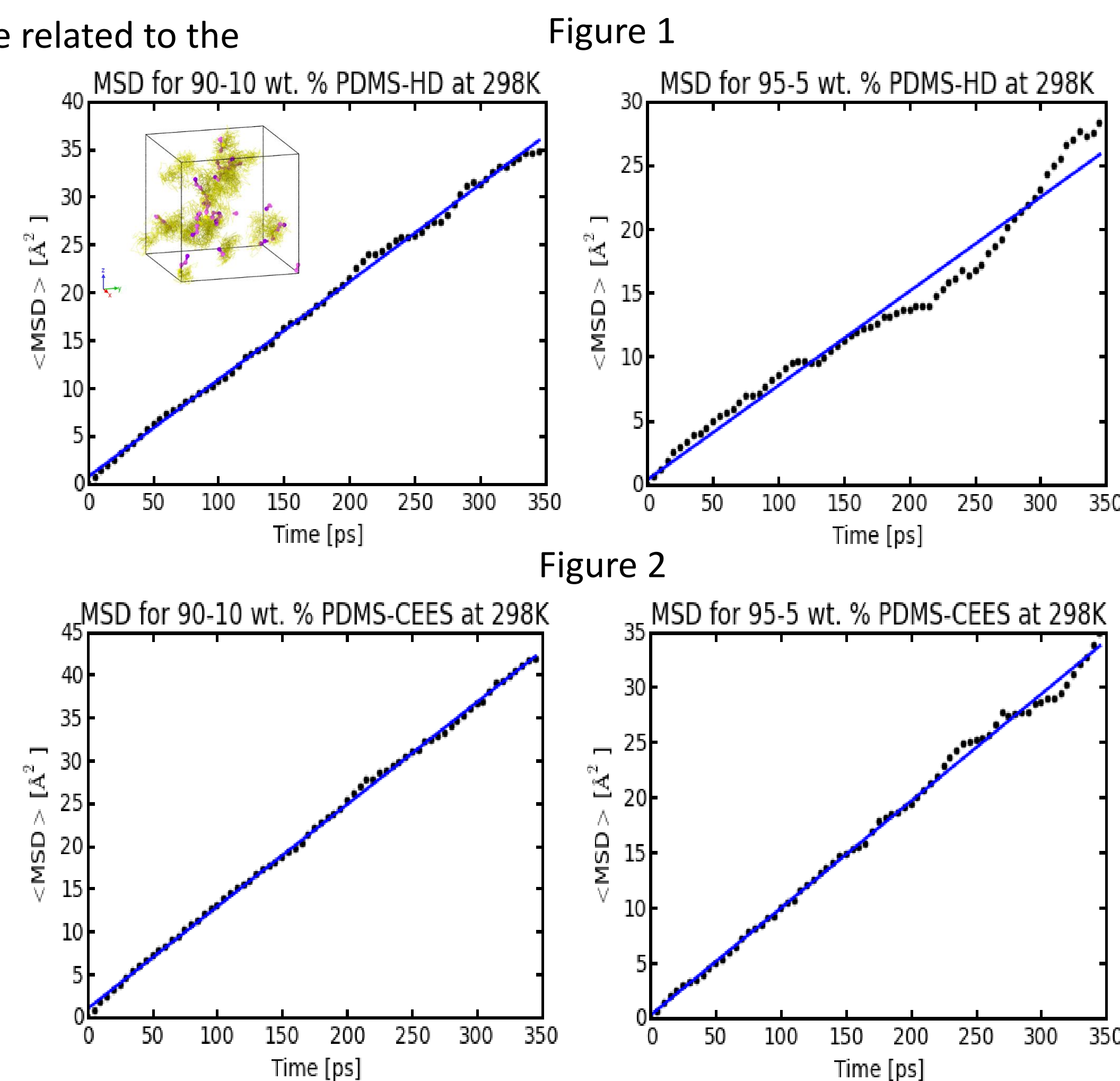


Table 1

PDMS/Penetrant	90-10 wt. %	95-5 wt. %	99-1 wt. %
HD	$1.01 \times 10^{-7} \frac{\text{cm}^2}{\text{s}}$	$7.37 \times 10^{-8} \frac{\text{cm}^2}{\text{s}}$	$1.86 \times 10^{-8} \frac{\text{cm}^2}{\text{s}}$
CEES	$1.20 \times 10^{-7} \frac{\text{cm}^2}{\text{s}}$	$9.71 \times 10^{-8} \frac{\text{cm}^2}{\text{s}}$	$2.93 \times 10^{-8} \frac{\text{cm}^2}{\text{s}}$

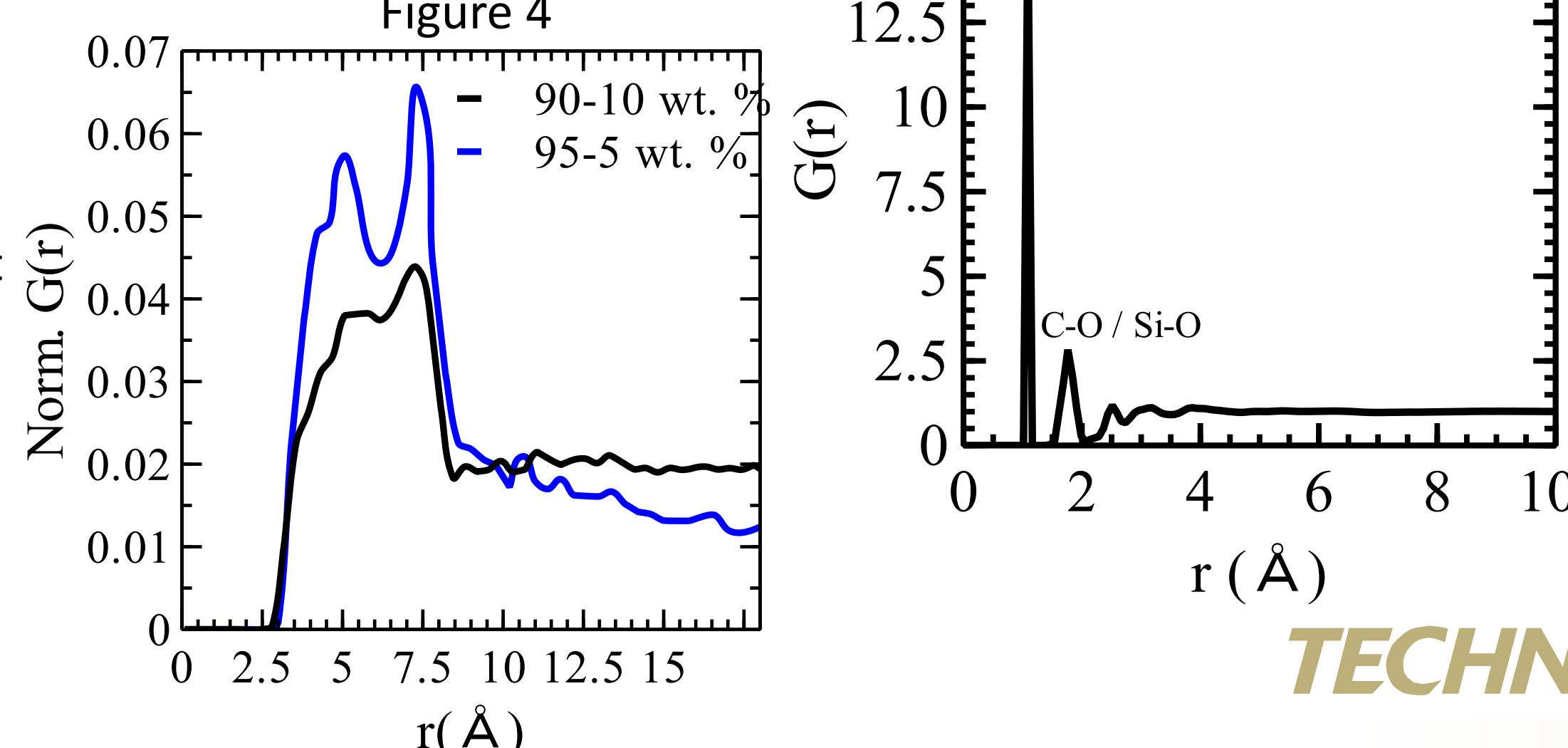
## Structural characterization

In order to gain some perspective on structural arrangement and possible mechanism associated with diffusive motion of molecules, one can look at structural correlations such as radial distribution functions (RDF). The RDF is given by:

$$G(r) = \frac{1}{n\rho} \sum_{i \neq j}^n \langle \delta(r + r_j - r_i) \rangle \quad \text{eq. 2}$$

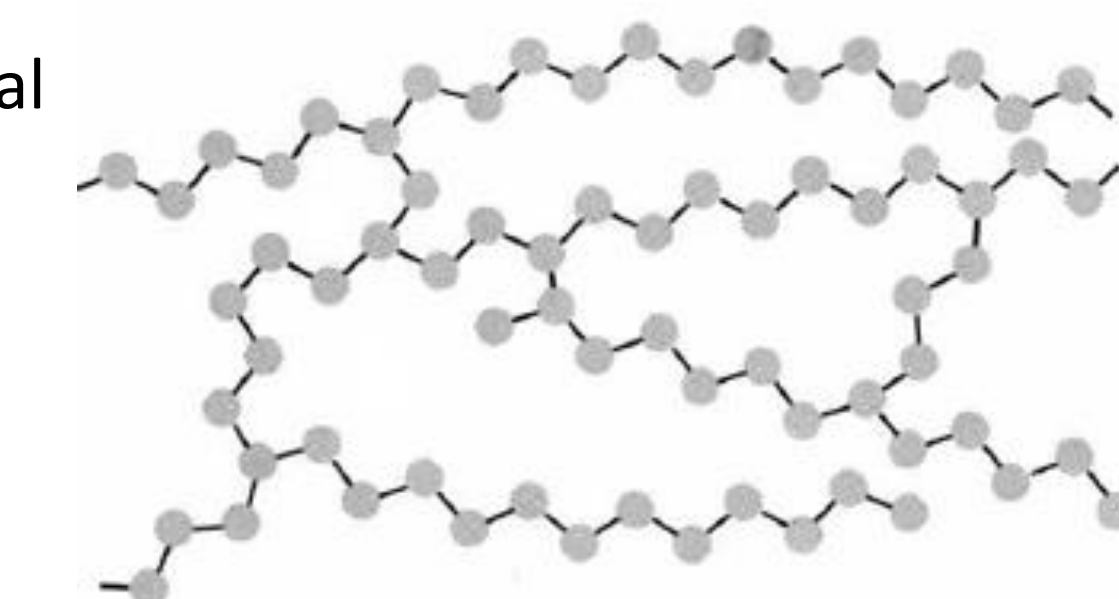
The total RDF for 90-10 wt. % PDMS with HD is shown in fig. 3 and is characteristic of an amorphous solid. The distribution is dominated By the C-H, C-O, and Si-O peaks.

Analysis of the Cl-Cl pair distribution function (see fig. 4) shows a decrease in weight percent of HD results in a peak at ~5 Å which corresponds to an intermolecular interaction between HD molecules. The reduction in diffusivities may correlate to this increased interaction.



## Future Efforts

The objective of this effort is to find key correlations between CWA and their simulants. Therefore, future MD simulations will survey the diffusivities of CEPS, MeS, GD, GB, DMMP, and VX in linear and cross-linked PDMS. We will also focus on temperature dependence of diffusivities. To improve our understanding, other structural characterization methods such as free-volume analysis and vibrational spectra will be employed.



The diffusivities obtained in this work are meaningful from a Fickian model perspective. However, MD can be used to obtain diffusivities for the Maxwell-Stefan model [3].

$$-\frac{\Delta \mu_i}{RT} = \sum_{i \neq j}^n \frac{x_i (v_i - v_j)}{D_{ij}}$$

Another capability available through MD is the ability to calculate thermodynamic quantities such as Gibbs excess free energy as a function of composition. This can be used with the Flory-Huggins/Flory-Rehner models to obtain solution solubility interaction parameters as a function of composition[4].

$$\frac{\Delta G_{\text{mix}}}{RT} = \sum_i^n n_i \ln \phi_i + \sum_{i \neq j}^N n_i \phi_j \chi_{ij}(\phi_i)$$

## Final Remarks

Preliminary investigation of HD and CEES in linear PDMS have shown concentration dependent diffusivities. Investigation of the Cl-Cl RDF in PDMS with HD demonstrates an increase in interaction between HD molecules.

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## Acknowledgements

The authors would like to thank Dr. Craig Knox for discussions relating the force field selection and HPC resources.